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(54) Moldings

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Abstract of th Disclosure: Moldings containing, as principal components, finely divided natural or synthetic materials and condensates of high molecular weight polycarboxylic acids and polyhydric alcohols, alkanolamines or polyamines can be produced for use as ceiling panels.

Moldings

The present invention relates to moldings which contain, as principal components, finely divided natural or synthetic materials and condensates of high molecular weight polycarboxylic acids and polyhydric alcohols, alkanolamines or polyamines

Moldings which essentially consist of finely divided natural or synthetic materials and binders, such as phenol/formaldehyde resins, furfural resins, amino-plasts or starch, are known. For example, EP-A 0 123 234 contains information on sound insulating boards which are composed mainly of mineral fibers, nonfibrous mineral fillers and starch and are coated with melamine/formaldehyde resins. However, the disadvantage of these moldings is that either their dimensional stability in the presence of high atmospheric humidity is not completely satisfactory and they absorb the atmospheric moisture and become deformed under their own weight, or, in the course of time, they release volatile, low molecular weight binder constituents, such as formaldehyde, which is disadvantageous particularly during use in closed rooms.

It is an object of the present invention to provide moldings which, on the one hand, have increased dimensional stability in the presence of high atmospheric humidity and, on the other hand, have a reduced or very low content of binders produced from readily volatile starting materials.

We have found that this object is achieved by the moldings defined at the outset, in which the condensates of high molecular weight polycarboxylic acids and polyhydric alcohols, alkanolamines or polyamines act as binders.

Suitable finely divided natural or synthetic materials are materials such as sands, kaolins, ground slate, mineral fibers such as mineral wool, plastics fibers, eg. polypropylene fibers, cellulose fibers, glass fibers or comminuted wood, such as wood fibers.

Particularly suitable high molecular weight polycarboxylic acids are polymeric polycarboxylic acids, such as polyacrylic acid, polymethacrylic acid, copolymers of acrylic and methacrylic acid or copolymers of acrylic and/or methacrylic acid with other monomers, such as esters of acrylic or methacrylic acid with C₁-C₂₄-alkanols, maleic acid or fumaric acid or other monomers, such as styrene or ethylene.

Polymeric polycarboxylic acids which contain, as polymerized units, not less than 5 but less than 50, preferably from 8 to 40 mol % based on the monomers constituting the polymeric polycarboxylic acids, of monomers which contain a carboxyl group, such as maleic acid, fumaric acid and in particular acrylic or methacrylic acid, are suitable. These polycarboxylic acids may contain, as polymerized units, from 50 to 95, preferably from 60 to 92 mol % of one or more monomers selected from the group consisting of styrene, ethylene, and in particular acrylates and methacrylates of alkanols of 1 to 6 carbon atoms.

These polycarboxylic acids have a K value of from 50 to 100 in dimethylformide (DMF) at 25°C. The K value is a relative viscosity number of a polymer, which is determined similarly to DIN 53,726. It characterises the mean molecular weight of the polymeric polycarboxylic acid. In this connection, the flow rate of a 0.1 % strength by weight solution of the polymeric polycarboxylic acid in DMF is measured, relative to the flow rate of pure DMF.

In many cases, particularly when the condensates are esters, for example low molecular weight alcohols, good results are obtained with polycarboxylic acids in which, as a rule, not less than 50, preferably not less than 90 mol % of their constituent monomers have one or more carboxyl functions. These polycarboxylic acids are known per se. They may contain minor amounts of other monomers, for example the abovementioned ones, as

polymerized units. High molecular weight polycarboxylic acids which are composed of only α, β -monoethylenically unsaturated carboxylic acids in polymerized form, in particular polyacrylic acid and polymethacrylic acid, are preferably used. These polymeric polycarboxylic acids in the form of their sodium salts advantageously have a K value of from 90 to 130 in water at 25°C. The flow rate of a 1% strength by weight solution of the sodium salt of polymeric polycarboxylic acid in water is measured relative to the flow rate of pure water.

The condensates may be esters and/or amides.

Suitable polyhydric alcohols in the case of esters include 2-hydroxymethylbutane-1,4-diol, trimethylolpropane, glycerol, glycol, polyvinyl alcohol, sorbitol, sugar or cellulose derivatives. Trimethylolpropane, glycerol or 2-hydroxymethylbutane-1,4-diol is preferably used.

Success is frequently achieved with high molecular weight polyalcohols. Examples of these are homo- and copolymers which contain polymerized simple esters of α, β -monoethylenically unsaturated carboxylic acids of 3 to 6 carbon atoms, such as acrylic and methacrylic acid, and polyhydric alcohols of 2 to 10 carbon atoms, such as 1,4-butanediol. Preferred comonomers are esters of α, β -monoethylenically unsaturated carboxylic acids of 3 to 6 carbon atoms and monohydric alcohols of 1 to 10 carbon atoms, in amounts of from 50 to 95, preferably from 70 to 95% by weight, based on the copolymers. These polymeric polyalcohols advantageously have a K value of from 40 to 80 in DMF at 25°C. The K value relates here to the flow rate of a 0.1% strength by weight solution of the polymeric polyalcohol in DMF relative to the flow rate of pure DMF. A substantial advantage of these high molecular weight polyalcohols is their high boiling point.

Particularly suitable alkanolamines are compounds which carry one or more amino groups and one or more

alcoholic OH groups on a hydrocarbon chain. Di- and triethanolamine are particularly important. Particularly suitable polyamines are diamines such as ethylenediamine or tetramethylenediamine.

5 The novel moldings are advantageously produced by a method in which the finely divided natural or synthetic materials are first added by mechanical mixing with an aqueous mixture of a binder. The mixture contains one or more high molecular weight polycarboxylic acids and one
10 or more polyamines, alkanolamines or polyhydric alcohols, generally in dissolved or dispersed form. The total amount of these substances in the mixture can be varied within wide ranges, in general from 0.05 to 40, in some cases up to 50% by weight, based on the aqueous mixture,
15 depending on the application. Depending on the viscosity, concentrations of more than 5% by weight are advantageous for coatings. These binder mixtures can usually be processed more than one month after their preparation. The excess binder is then usually separated off (for
20 example by filtration under suction or pressing out), and the slurry-like material which results is molded and then dried at from 100 to 250°C, drying being accompanied by esterification or amide formation in a condensation reaction, which is promoted by drying under pressure.
25 The high molecular weight polycarboxylic acids and the polyhydric alcohols, alkanolamines and polyamines are preferably used in amounts such that the number of acid functions in relation to the total number of alcoholic hydroxyl and amine functions is in a ratio of from 4:1 to
30 1:4, advantageously from 2:1 to 1:2 to one another. Equivalence, ie. a 1:1 ratio is particularly advantageous.

35 Polymeric polycarboxylic acids which contain not less than 5 but less than 50 mol %, based on the monomers constituting the polymeric carboxylic acids, of polymerized monomers which possess a carboxyl group are, as a rule, insoluble in water under standard conditions

and are therefore used as an aqueous polymer dispersion. These are obtainable in a conventional manner, for example by free radical emulsion polymerization. The same usually applies to polymeric polyalcohols which contain less than 75 mol%, based on the monomers constituting them, of polymerized monomers which have an alcoholic OH group.

The binder content, based on the total mass of the moldings and calculated as dry material, is preferably from 0.5 to 15% by weight, the water absorptivity of the binder in the dry state being usually less than 5% by weight, based on the dry mass of the binder.

In an alternative method of production, moldings which have been produced, for example, by pressing the finely divided natural or synthetic materials are coated with the aqueous mixtures containing one or more high molecular weight polycarboxylic acids and one or more polyamines, alkolamines or polyhydric alcohols in general in dissolved or dispersed form, and are then dried. Coating should be taken to include processes for applying the mixtures to the surface of the molding, such as impregnating, spraying and immersing. Basic moldings which are composed of natural or synthetic finely divided materials and other binders, for example starch, can also be treated in a corresponding manner by coating with the condensates and drying.

The novel moldings are preferably produced in sheet-like form and used, for example, as ceiling panels in wet rooms. They are distinguished by reduced water absorption, high internal strength and, consequently, increased dimensional stability.

It may be advantageous also to incorporate commercial flocculants, for example copolymers of 70% by weight of acrylamide and 30% by weight of diethylaminoethyl acrylate or water-repellent assistants, such as stearyl diketene or polysiloxanes, or other conventional assistants, eg. an aqueous solution of aluminum sulfate

as a precipitant, during the preparation of the starting slurry composed of the finely divided materials and the aqueous binder.

In th Examples, parts and percentages are by weight, unless stated otherwise.

EXAMPLES

Investigation of various novel moldings F1 to F17

a) Determination of the dimensional stability

Test specimens having the following dimensions were produced by abrading the side facing away from the sieve during production of the molding (which will be described in detail below):

length 250 mm
width 50 mm and
height 15 mm.

The moldings thus obtained were placed horizontally flat on a surface, supported only near each of the 50 mm wide end edges, in a room held at 38°C and 99% relative humidity and were loaded with a weight of 1 kg mass at their geometric center. The load was left in place for a certain time and then removed to measure the sag of the test specimen, ie. the lowering of the center relative to the starting position.

b) Strength

Test specimens having the dimensions

length 17 cm
width 2 cm and
height 2 cm

were placed horizontally on a surface, supported only near each of the end edges of the broad side, under standard conditions of temperature and humidity, and were subjected to a continuously increasing force in their geometric center. The force applied when fracture occurs is a measure of the strength.

c) Tensile force

The tensile force was determined according to DIN 53455.

F1: 250 g of mineral wool were stirred into a mixture of 5 kg of water, 360 g of polyacrylic acid (K value of the Na salt at 25°C in water = 110), 140 g of 2-hydroxymethylbutane-1,4-diol and 9.2 g of a polysiloxane.

5 Thereafter, 4 g of a 10% strength by weight aqueous solution of a commercial copolymer of 70% by weight of acrylamide and 30% by weight of diethylaminoethyl acrylate were added as a flocculant. 20% of the
10 resulting slurry were then uniformly distributed in a strainer (sieve area 25 cm x 5 cm) and coarsely dewatered by slightly reducing the pressure while simultaneously pressing with an applied perforated plate (25 cm x 5 cm, 0.1 bar), so that a moist raw panel having a thickness of 18 mm and a water content of from 40 to 80% by weight was obtained. This
15 was dried at 180°C in a through-circulation drier.

Dimensional stability = 1 mm sag after 260 h

F2: As for F1, except that 100 g of kaolin were added in addition to the mineral wool.

Dimensional stability = no measurable sag after 360 h

20 F3: As for F1, except that 150 g of trimethylolpropane were used as the polyhydric alcohol.

Dimensional stability = 3 mm sag after 56 h

F4: As for F1, except that 128 g of glycerol were used as the polyhydric alcohol.

25 Dimensional stability = 3 mm sag after 120 h

F5: A commercial 16 mm thick mineral fiber panel containing starch as the binder was used as the basic
molding and was coated on the decorative surface with an aqueous solution of 36 g of polyacrylic acid (having a K
30 value of the Na salt at 25°C in water = 110) and 14 g of 2-hydroxymethylbutane-1,4-diol in 200 g of water by application with a brush (amount applied: 100 g of dry material/m²) and was dried for 15 min at 150°C in a through-circulation drier. A test specimen having the dimensions
35 250 mm x 50 mm x 16 mm was then cut therefrom and was tested for dimensional stability in the manner described. The test was then repeated with the uncoated basic molding.

Dimensional stability = fracture after 21 h (uncoated)

1 mm sag after 192 h (coated)

F6: As for F5, except that a mixture of 6.2 g of glycerol and 7.4 g of trimethylolpropane was used as the polyhydric alcohol.

Dimensional stability = 2 mm sag after 154 h

F7: 96 g of finely divided wood and cellulose fibers, 24 g of finely divided polypropylene fibers, 3 l of water, 180 g of polyacrylic acid (K value of the Na salt at 25°C in water = 110) and 45 g of trimethylolpropane were mixed to give a fiber slurry, into which 24 g of an 8% strength by weight aqueous emulsion of stearyl diketene and 4 g of a 10% strength by weight aqueous solution of a commercial copolymer of 70% by weight of acrylamide and 30% by weight of diethylaminoethyl acrylate were additionally stirred in the stated order. The material was then distributed uniformly in a strainer (25 cm x 25 cm) and was coarsely dewatered as described for F1. The raw panel obtained in this manner was additionally predried in a microwave oven to a residual water content of 15% by weight. Final drying was then carried out in a heated press at 20°C and at 50 kp/cm². The pressing time was 90 s.

Tensile force: 12 N/mm²

F8: As for F7, except that 38 g of glycerol was used as the polyhydric alcohol.

Tensile force: 9.5 N/mm²

F9: 50 g of finely divided wood fibers were stirred with 19 g of an 8% strength by weight aqueous emulsion of stearyl diketene and then dried at 120°C for 15 min. A solution of 8 g of polyacrylic acid (K value of the Na salt at 25°C in water = 110) and 3 g of 2-hydroxymethylbutane-1,4-diol in 40 g of water was then stirred in. Thereafter, drying was carried out, again at 120°C for 15 min, and the material was pressed in a mold (20 cm x 20 cm) at 220°C and 50 kp/cm² for 90 s in a heated press. Fiber boards having a thickness of 4 mm were obtained.

Tensile force: 8.5 N/mm²

5 F10: A solution of 58 g of polyacrylic acid (K value of the Na salt at 25°C in water = 110) and 21 g of 2-hydroxymethylbutane-1,4-diol in 200 g of water was stirred with 1400 g of standard sand (according to DIN 1164, Part 7) and a mold (17 cm × 2 cm × 2 cm) was filled with this mixture with compaction. Drying was then carried out for 2 h at 180°C.

Strength: 10.7 kg/cm²

10 F11: 250 g of mineral wool was stirred into a mixture of 7 kg of water, 40.2 g of a commercial 30% strength by weight aqueous polymer dispersion of a polymeric polyalcohol which consisted, in polymerized form, of 80 parts by weight of methyl methacrylate and 20 parts by weight of a hydroxypropyl acrylate (K value at 25°C in DMF = 50), 20.1 g of a commercial 40% strength by weight aqueous polymer dispersion of a polymeric polycarboxylic acid which consisted, in polymerized form, of 60 parts by weight of methyl methacrylate, 30 parts by weight of n-butyl acrylate and 10 parts by weight of methacrylic acid (K value at 25°C in DMF = 70) and 16 g of a polysiloxane.

20 4 g of a 10% strength by weight aqueous solution of a commercial copolymer of 70% by weight of acrylamide and 30% by weight of diethylaminoethyl acrylate were then added as a flocculant. Thereafter, 20% of the resulting slurry was uniformly distributed in a strainer (surface area 25 cm × 5 cm) and coarsely dewatered by slightly reducing the pressure while simultaneously pressing with an applied perforated plate (25 cm × 5 cm, 0.1 bar), so that a moist raw panel having a thickness of 18 mm and a water content of from 40 to 80% by weight was obtained. This was dried at 180°C in a through-circulation drier. Dimensional stability = 2 mm sag after 213 h

30 F12: As for F11, except that a solution of 3.15 g of trimethylolpropane and 28 g of water was used instead of the aqueous dispersion of the polymeric polyalcohol.

35 Dimensional stability = 4 mm sag after 128 h

F13: A commercial 16 mm thick mineral fiber panel containing starch as the binder was used as the basic molding and was coated on the decorative surface with an aqueous mixture of 500 g of a commercial 30% strength by weight aqueous polymer dispersion of a polymeric polycarboxylic acid which, in polymerized form, consisted of 70 parts by weight of methyl methacrylate and 30 parts by weight of methacrylic acid (K value at 25°C in DMF = 70) and 500 g of a commercial 30% strength by weight aqueous polymer dispersion of a polymeric polyalcohol, which, in polymerized form, consisted of 80 parts by weight of methyl methacrylate and 20 parts by weight of hydroxypropyl acrylate (K value at 25°C in DMF = 50) by application with a brush (amount applied: 100 g of dry material/m²) and was dried for 50 min at 150°C in a through-circulation drier. A test specimen having dimensions 25 mm x 50 mm x 16 mm was then cut therefrom and was tested for dimensional stability in the manner described. The test was then repeated with the uncoated basic molding.

Dimensional stability = fracture after 24 h (uncoated)
3 mm sag after 271 h (coated)

F14: As for F13, except that a solution of 4.5 g of diethanolamine in 350 g of water was used instead of the aqueous dispersion of the polymeric polyalcohol.
Dimensional stability = 3 mm sag after 220 h

F15: 90 g of finely divided wood fibers and cellulose fibers, 20 g of finely divided polypropylene fibers, 8 l of water, 12 g of a commercial 30% strength by weight aqueous polymer dispersion of a polymeric polycarboxylic acid which, in polymerized form, consisted of 80 parts by weight of methyl methacrylate and 20 parts by weight of methacrylic acid (K value at 25°C in DMF = 70) and 8 g of a commercial 30% strength by weight aqueous polymer dispersion of a polymeric polyalcohol, which, in polymerized form, consisted of 90 parts by weight of methyl methacrylate and 10 parts by weight of

- hydroxypropyl acrylate (K value at 25°C in DMF = 50) were mixed to give a fiber slurry, into which additionally 25 g of a 10% strength by weight aqueous aluminum sulfate solution and 4 g of a commercial copolymer of 70% by weight of acrylamide and 30% by weight of diethylaminoethyl acrylate were stirred. Thereafter, the mass was uniformly distributed in a strainer (25 cm x 25 cm) and coarsely dewatered as described in F11. The raw panel obtained in this manner was additionally predried in a microwave oven to a residual water content of 15% by weight. Final drying was then carried out in a heated press at 20°C and at 50 kp/cm². The pressing time was 30 s. Tensile force: 11.5 N/mm²
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- 10
- F16: As for F15, except that a solution of 0.1 g of triethanolamine in 6 g of water was used instead of the aqueous dispersion of the polymeric polyalcohol. Tensile force: 8.5 N/mm²
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- F17: 50 g of finely divided wood fibers were stirred with 19 g of an 8% strength by weight aqueous emulsion of stearyl diketenes and drying was then carried out at 120°C for 15 min. A mixture of 4 g of a commercial 40% strength by weight aqueous polymer dispersion of a polymeric polycarboxylic acid which, in polymerized form, consisted of 60 parts by weight of methyl methacrylate, 30 parts by weight of n-butyl acrylate and 10 parts by weight of methacrylic acid (K value at 25°C in DMF = 70) and 2 g of a commercial 30% strength by weight aqueous polymer dispersion of a polymeric polyalcohol which, in polymerized form, consisted of 90 parts by weight of methyl methacrylate and 10 parts by weight of hydroxypropyl acrylate (K value at 25°C in DMF = 50) was then stirred in. Drying was then carried out once again at 120°C for 15 min and the mass was pressed in a mold (20 cm x 20 cm) at 220°C and 50 Kp/cm² for 90 s, in a heated press. Fiber panels having a dimension of 4 mm were obtained. Tensile force: 10 N/mm²
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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A molding which contains, as the principal components, finely divided natural or synthetic materials and condensates of high molecular weight polycarboxylic acids and polyhydric alcohols, alkanolamines or polyamines.
2. A molding as claimed in claim 1, which contains from 0.5 to 15% by weight, based on the total weight, of condensates of high molecular weight polycarboxylic acids and polyhydric alcohols, alkanolamines or polyamines.
3. A molding as claimed in claim 1, which contains condensates during whose condensation reaction the high molecular weight polycarboxylic acids and the polyhydric alcohols, alkanolamines or polyamines are used in amounts such that the number of acid functions is equivalent to the total number of alcoholic hydroxyl and amine functions.
4. A molding as claimed in claim 1, which contains condensates of polymeric polycarboxylic acids which contain not less than 5 but less than 50 mol%, based on the monomers constituting the polymeric polycarboxylic acids, of polymerized monomers which possess a carboxyl group.
5. A molding as claimed in claim 4, which contains condensates of polymeric polycarboxylic acids, the polycarboxylic acids having a K value of from 50 to 100 in dimethylformamide at 25°C.
6. A molding as claimed in claim 1, which contains condensates of high molecular weight polycarboxylic acids and polymeric polyalcohols whose K value is from 40 to 80 at 25°C in dimethylformamide.
7. A molding as claimed in claim 1, which contains condensates of high molecular weight polycarboxylic acids and trimethylolpropane, glycerol, 2-hydroxymethylbutane-1,4-diol, diethanolamine, triethanolamine, ethylenediamine or tetramethylenediamine.
8. A molding as claimed in claim 1, which contains

condensates of polymeric polycarboxylic acids which contain not less than 50 mol% of the polymerized monomers which have a carboxyl group.

9. A molding as claimed in claim 8, wherein the high molecular weight polycarboxylic acids are selected from the group consisting of polyacrylic acid, polymethacrylic acid and mixtures thereof.

10. A molding as claimed in claim 8, which contains condensates of polymeric polycarboxylic acids whose sodium salts have a K value of from 90 to 130 in water at 25°C.

11. A molding as claimed in claim 8, which contains condensates whose alcoholic component is trimethylolpropane, glycerol or 2-hydroxymethylbutane-1,4-diol.

12. A process for the production of a molding as claimed in claim 1, wherein an aqueous mixture which contains one or more high molecular weight polycarboxylic acids and one or more polyamines, alkanolamines or polyhydric alcohols is first added to the finely divided natural or synthetic materials as a binder by mechanical mixing, the excess binder is separated off and the resulting material is then molded and dried at from 100 to 250°C.

13. A process for the production of a molding as claimed in claim 1, wherein a shaped article premolded by pressing finely divided natural or synthetic materials is coated with an aqueous mixture containing one or more high molecular weight polycarboxylic acids and one or more polyamines, alkanolamines or polyhydric alcohols and then dried at from 100 to 250°C.

14. A process for the production of a molding as claimed in claim 1, wherein the basic molding, which is composed of natural or synthetic finely divided materials and a binder, is coated with an aqueous mixture containing one or more high molecular weight polycarboxylic acids and one or more polyamines, alkanolamines or polyhydric alcohols, and is then dried at from 100 to

250°C.

15. A ceiling panel made from a molding as claimed in claim 1.